Cadmium Mobility and Bioaccumulation by Willow

by Larry P. Gough, Paul J. Lamothe, Richard F. Sanzolone, James G. Crock, Andrea L. Foster

Abstract

Biogeochemical investigations of cadmium (Cd) bioavailability are being conducted in mineralized and non-mineralized areas in order to understand the mechanisms by which willow *(Salix)* bioaccumulates Cd, and ultimately to evaluate the importance of this phenomenon to the health of browsing animals. Within Denali National Park and Preserve (Denali) sites included the historic Mt. Eielson and Kantishna Mining Districts that contain both disturbed and undisturbed mineralized areas. Soils collected included the A, B, and C horizons. Plants collected included diamondleaf and grayleaf willow as well as green alder, feather moss, and soil lichen. Willow growing in soils developed from base metal-rich bedrock bioaccumulated Cd in concentrations 4- to 10-times higher than willow growing in non-mineralized soil. Cd levels in willow were as much as 10-100 times greater than those found in other plants collected from the same area. Mineralized areas are particularly important loci for the natural occurrence of potentially harmful levels of Cd in browse willow.

Introduction

In this study we compared the mobilization and uptake of Cd by willow *(Salix)* and other plant species in a non-mineralized area (Yukon-Tanana Upland, YTU) and a mineralized area (Mt. Eielson/Kantishna, Denali), *(Figures 1 and 2)*. Cd occurs naturally in certain minerals (e.g., sphalerite) and in plants it is a nonessential heavy metal and a powerful enzyme inhibitor. In ruminants, Cd, copper (Cu), and zinc (Zn) are often mutually antagonistic: exposure to Cd lowers Cu status and exposure to Zn lowers Cd status *(Underwood and Suttle, 1999; Frank et al., 2000)*. All three metals induce the production of metallothionein, a group of proteins that bind the metals in animal tissue. Unlike Cu and Zn, Cd has a biological half-life measured in years (thus potentially accumulating over time), showing highest concentrations in kidney tissue. In a study of white-tailed ptarmigan in Colorado, Larison et al. (2000) found that a diet of willow buds, having mean Cd concentrations as low as 2.1 ppm (dry weight basis), resulted in renal tubular damage and increased chick mortality. They proposed that non-anthropogenic Cd poisoning might be more widespread than previously suspected. We hypothesize that Cd bioaccumulation by willow, in areas naturally high in Cd, may be detrimental to the health of moose *(Gough et al., 2002)* by being directly toxic (nephropathy; poor bone construction) and/or by inducing Cu deficiency *(Frank et al., 2000)*.

Figure 1. Map of study areas in Alaska. The area within DENA included the Mt. Eielson and Kantishna mining districts.

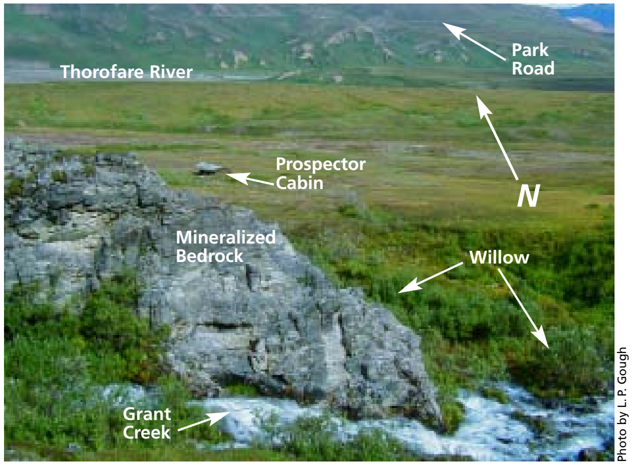

Figure 2. The Mt. Eielson Mining District with Grant Creek and typical mineralized bedrock in the foreground, a historic cabin dating to the days of mineral prospecting in the district in the near background, and the Thorofare River and the park road in the far background.

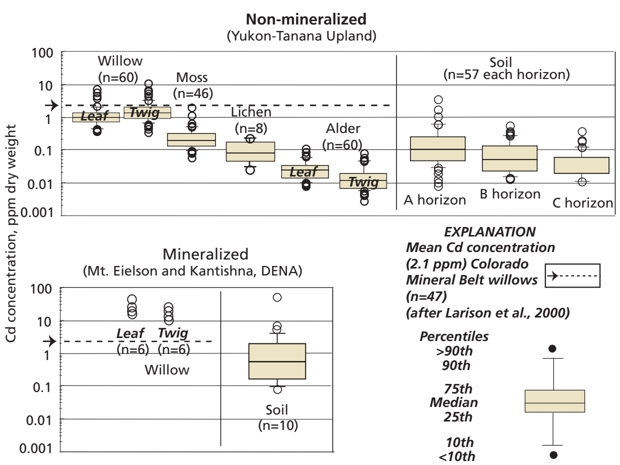

Figure 3. Box plots of the concentration of Cd (plotted on a log scale) in plants and soils from a non-mineralized area (Yukon-Tanana Upland) and from the mineralized Mt. Eielson and Kantishna Mining Districts, Alaska. Arrows indicate mean Cd concentration (2.1 ppm) in willow found to be toxic to ptarmigan in the Colorado Mineral District *(Larison et al. 2000).*

Methods

Samples of plants, soils, and waters were collected from 57 non-mineralized (in YTU) and six mineralized sites (in Denali) *(Figure 1)*. Sites were in both boreal forest and tundra vegetation zones. Plants collected included the stems and leaves of *Salix planifolia* ssp. *pulchra* (diamondleaf willow) and *S. glauca* (grayleaf willow) as well as green alder *(Alnus crispa)*, feather moss *(Hylocomium splendens)*, and a soil lichen *(Cetraria islandica)*. Soils collected were mainly mature, silty Inceptisols and Gelisols from moderately- to well-drained southerly exposures, and possessed a mixture of residuum and loess.

Chemical analyses were performed in the Denver, Colorado Laboratories of the U.S. Geological Survey *(Taggart 2002)*. Analytical duplicates, blanks, and standard reference materials were analyzed to assess data reliability. Total element concentrations were determined by inductively coupled plasma-mass spectrometry (ICP-MS) following four-acid total dissolution. Powder X-ray diffraction analysis was used to determine soil mineralogy. The speciation of Cd in willow is being investigated using X-ray absorption fine structure (XAFS) spectroscopy *(Foster et al. 2004)*.

The mode of occurrence of Cd in soil was determined by sequential-partial extraction using the methods of Tessier et al. *(1979)*, Chao and Zhou *(1983)*, and Hall et al. *(1996)*. Extractions are identified as follows: Fraction I—1 M magnesium chloride, pH 7.0 (target is water-soluble, adsorbed and exchangeable ions); Fraction II—1 M sodium acetate in acetic acid buffered to pH 5 (target is carbonate mineral phases); Fraction III—0.25 M hydroxylamine hydrochloride in 0.25 N hydrochloric acid (target is amorphous Fe and Mn oxides); Fraction IV—4 N hydrochloric acid in boiling water bath with occasional agitation for 45 minutes (target is crystalline iron (Fe), manganese (Mn), and aluminum (Al) oxides, secondary and mono-sulfides, some hydrolysis of organic matter, and minor attack on edges of silicate minerals); and Fraction V—four-acid (hydrofluoric, hydrochloric, perchloric, and nitric) total dissolution of residue (target is silicates and other residual minerals).

Surface water at each site (when available) was collected, filtered (<0.45 μm) and acidified with ultrapure nitric acid. Measurements of pH, conductivity, alkalinity, and temperature were made at each site. Multi-element determinations on water samples were made using ICP-MS.

Results

The bioaccumulation of Cd appeared to be pervasive within the genus *Salix* (willow). Cd concentrations in leaf and stem (twig) material are commonly similar *(Figure 3)*. Cadmium concentrations in leaf can exceed 30-35 times that of soil *(Granel et al. 2002)*. The efficacy of willow to bioaccumulate Cd is due to a number of attributes including high biomass production and high water-use *(Gough et al. 1999)*. However, these features alone are inadequate to explain Cd bioaccumulation because other woody species (e.g., poplar) also have these traits but do not necessarily accumulate Cd. We hypothesize that willow might possess a metal-specific transport molecule that, if not unique to willow, is either concentrated in willow or functions more efficiently in willow. Our work thus far has shown that willow tissue (native and plantation-grown), examined using XAFS, possesses both an "inorganic" (Cd complexed to oxygen or nitrogen) and an "organic" (sulfur-bonded Cd) form *(Foster et al. 2004)*.

Total soil Cd concentrations ranged from about 0.009 to 4.5 ppm (the A, B, and C soil horizons combined) in the non-mineralized area and from 0.09 to 51 ppm in the Mt. Eielson/Kantishna area (for comparison, crustal abundance is approximately 0.1 ppm) *(Emsley 1991)*. In the non-mineralized areas, no difference in total Cd was seen in soils developed over different lithologic (bedrock) units. In mineralized areas, Cd mean concentrations varied by mineralization type with the greatest Cd concentrations at sites containing sphalerite. Cd concentrations decrease with depth at both mineralized and non-mineralized sites, with the means in mineralized areas larger than in non-mineralized areas *(Figure 3)*. At individual non-mineralized sites, this decrease in concentration with depth is consistent, whereas at individual mineralized sites this trend was not so apparent. The decrease in Cd concentration with depth correlates with soil organic matter in non-mineralized soils (r = 0.61).

In order to better understand the physical and chemical association of Cd in mineralized soils, a sequence of five extractions were applied to selected samples. The scheme used extractants that increase in the aggressiveness with which they attack soil exchange sites and mineral structure. Such schemes provided insight into the speciation of trace elements in solid phases. The extraction scheme removed an average of 91% of the total soil Cd. Operationally defined speciation could be evaluated by looking at major phase constituents released in each extraction *(Figure 4)*. For example, the second extraction targeting carbonate minerals removed 32% of the total calcium (Ca) in a sample high in calcite and 54% of the total Cd. Cadmium removed by the first three extractions ranges from 55 to 100% (mean 76%) of the total. Figure 4 shows that a greater percentage of the total soil Cd was more available at the surface than at depth in these soils, especially in non-mineralized areas.

The range in concentration of Cd in surface waters, collected from Grant Creek, Mt. Eielson, was 0.06-0.08 µg/L (n= 4). In contrast, Cd concentrations in the non-mineralized YTU were all <0.02 µg/L (n=41), the analytical detection limit *(Bronwen Wang, USGS Alaska Science Center, personal communication)*. In the mineralized areas, elevated Cd concentrations in water were found at sites having high Cd in soils; however, soils elevated in Cd did not always have detectable Cd in associated waters.

The total median Cd concentration (dry weight basis) in willow (n=6) from mineralized areas was 12.5 ppm in leaves and 10.5 ppm in twigs. Willow (n=60) from the YTU had median leaf and twig concentrations of about 1.0 ppm and 1.5 ppm, respectively *(Figure 3)*. In contrast, leaf and twig material from another shrub browse species (alder) had a median Cd value of <0.04 ppm. Plantation-grown willow, cultivated under controlled conditions that were dosed with 0.18 mM (20 ppm Cd) Cd-nitrate, had similar Cd levels as willows collected in mineralized areas.

Both diamondleaf and grayleaf willow are significant bioaccumulators of Cd in their leaf and twig tissue. Even in non-mineralized areas, willow was found to have 10- to as much as 100-times the concentration of Cd compared to several other plant species, including moss and lichen.

Discussion and Management Implications

Both diamondleaf and grayleaf willow are significant bioaccumulators of Cd in their leaf and twig tissue. Even in non-mineralized areas, willow was found to have 10- to as much as 100-times the concentration of Cd compared to several other plant species, including moss and lichen. In the mineralized areas of Denali that were examined, the Cd levels in willow generally exceeded 10 ppm; the median concentration in non-mineralized areas was about 1 ppm. Willow leaves high in Cd are shed in the fall and upon decay a large proportion of the Cd is released and sorbed onto cation exchange sites such as clays and soil organic matter. In this form it is readily available for uptake by willow explaining the importance of biocycling to the distribution of Cd in cold, high latitude soils.

Diamondleaf and grayleaf willow are found in a variety of habitats. Typically they occur in upland boreal forests, as part of the shrub understory, and in dense, nearly uniform stands in alpine and arctic tundra. Willow palatability and browse preference is apparently linked to the presence or absence of specific tannins and phenyl glycosides *(Molvar et al. 1993)* and these two willow species are a favorite browse for moose throughout the year. Because willow is a bioaccumulator of Cd, and because Cd is potentially toxic and known to have a long residence time in mammalian kidney tissue, we find it interesting to speculate on the possible long-term health effects of Cd in natural, Cd-rich areas. In Table 1 we compare the concentration of Cd, Cu, and Zn in the liver and kidney of 17 road-kill moose, collected in a non-mineralized area of Alaska, to diseased moose from Sweden *(Frank et al. 2000)*. Concentrations of all three metals were lower in both liver and kidney tissue in the Alaska samples. Publication of metal levels in possibly diseased moose from Alaska are pending *(Julie Maier, University of Alaska, personal communication)*.

Although a direct aetiological connection between high

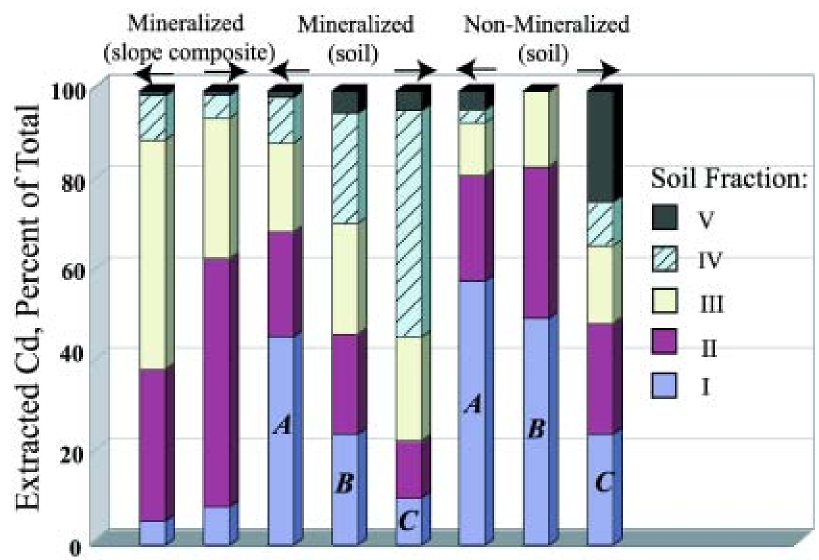

Figure 4. Sequential partial-extraction of two samples of unconsolidated slope material and six soil samples from Mt. Eielson, Denali. See Results section for a description of the five fractions. A, B, and C indicate soil horizon samples.

Cd in browse, high Cd in renal tissue, and the well-being of ptarmigan has been demonstrated *(Larison et al. 2000)*, its connection to the health of moose remains a research question. Game management practices should be cognizant of this potential health impact, however, especially in areas of broad-regional mineralization or where base-metal mine-dumps are revegetated with willow as these areas might be expected to be high in bioavailable Cd.

Acknowledgements

The USGS Mineral Resources Program provided funding for this work. We thank Monique Adams, Zoe Ann Brown, and Cathy Ager for the chemical analysis of samples and Steve Sutley for the soil mineralogical evaluations. Cathy was also responsible for conducting the willow plantation experiment. We are especially grateful to William Collins, Alaska Department of Fish and Game, for providing moose liver and kidney tissue for analysis.

	Minimum	Maximum	Mean
Moose liver	ALASKA (n = 4)		
Cd, mg/kg	0.02	5.7	1.7
Cu, mg/kg	0.51	7.4	3.2
Zn, mg/kg	16	56	28
Moose liver	SWEDEN (n = 14)*		
Cd, mg/kg	0.68	4.4	1.9
Cu, mg/kg	3.2	28	11
Zn, mg/kg	22	151	67
Moose kidney	ALASKA (n = 17)		
Cd, mg/kg	0.27	6.5	2.3
Cu, mg/kg	2.2	3.5	2.8
Zn, mg/kg	17	29	21
Moose kidney	SWEDEN (n = 14)*		
Cd, mg/kg	5.1	27	12
Cu, mg/kg	2.3	26	5.5
Zn, mg/kg	30	86	49

*From Frank et al. 2000

Table 1. The concentration (mg/kg, wet weight basis) of Cd, Cu, and Zn in moose liver and kidney tissue from Alaska and Sweden. All Alaska samples are from road-kill animals collected in the Kenai Peninsula and the Matanuska-Susitna Valley; samples from Sweden are from "affected animals" showing Cu-deficiency disease symptoms *(Frank et al., 2000).*

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